FOREIGN TECHNOLOGY DIVISION

STUDIES ON THE DYNAMIC MECHANICAL PROPERTIES
OF THE COMPOSITE MODIFIED DOUBLE-BASE PROPELLANT

by

Zhou Zhou, Jia Zhanning and Zhou Qihuai

HUMAN TRANSLATION

FTD-ID(RS)T-0328-86   29 May 1986

MICROFICHE NR: FTD-86-C-001886
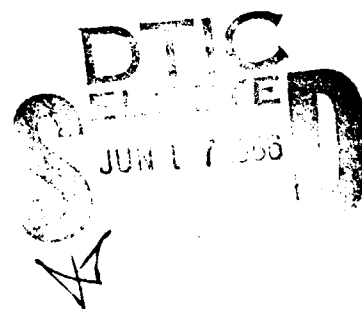
STUDIES ON THE DYNAMIC MECHANICAL PROPERTIES OF
THE COMPOSITE MODIFIED DOUBLE-BASE PROPELLANT

By: Zhou Zhou, Jia Zhanning and Zhou Qihuai

English pages: 20

Source: Binggong Xuebao, Vol. 2, Nr. 2, May 1985,
         pp. 49-58

Country of origin: China
Translated by: SCITRAN
                F33657-84-D-0165
Requester: FTD/TQTA
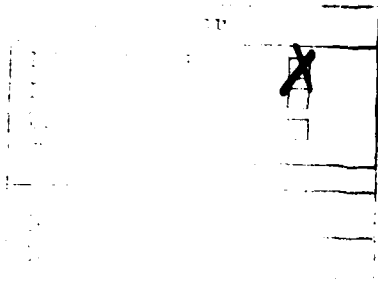Approved for public release; Distribution unlimited.

GRAPHICS DISCLAIMER

All figures, graphics, tables, equations, etc. merged into this
translation were extracted from the best quality copy available.

A-1

i

STUDIES ON THE DYNAMIC MECHANICAL

PROPERTIES OF THE COMPOSITE MODIFIED

DOUBLE-BASE PROPELLANT*

Zhou Zhou, Jia Zhanning and Zhou Qihuai**

Abstract

The dynamic mechanical properties of the composite modified double-base (CMDB), double-base (DB) and polyvinyl chloride (PVC) composite propellants were measured respectively with a Rheovibron viscoelastometer. The effects of three kinds of solid fillers[aluminium (Al), ammonium perchlorate (AP) and cyclotetraethylenetetranitramine (HMX)] and the different kinds and contents of plasticizers[triacetin(TA), ortho-dibutyl phthalate(DBP)and nitroglycerine(NG)]on the dynamic mechanical properties of the double-base binder were studied. The dynamic mechanical data and spectrums on these ingredients have been obtained at a fixed frequency(3Hz)and a broad range of temperature. At the same time, the impact strengths of the CMDB propellant, the double-base binder and the pvc propellant were also measured at a broad range of temperature. Experimental conclusions have been obtained that the dynamical mechanical properties of the CMDB propellant lie between the DB and PVC composite propellants and depend on its binder system, and that the CMDB propellant has the specific properties of both higher mechanical damping and a strong β relaxation at low temperature.

From related publications in the U.S. since the early

1960's, dynamic mechanical properties of solid propellants [1]

have been studied using various dynamic measurement instruments [2].

Recently, similar works have also been done in England.

However, in the U.S., most of the researchers have concentrated

on complex propellants. There have been no studies reported

on the dynamic mechanical properties of CMDB propellants.

In China, the dynamic property measurements of solid propellants

**Deceased.

1

using the twisting method and the vibrating spring method have been attempted.

In this paper a study of the dynamic properties, as well as the effect of the composition on the mechanical properties of CMDB propellants, is discussed by using a viscoelastometer.

1. Samples and Experimental Method

1.1 Samples

The detailed compositions of the samples are listed in Tables 1.1 - 1.3.

1.2 Experimental Method

1.2.1 Dynamic Experimental Method

The dissipation angle δ (i.e. the phase difference between the sinusoidal strain and the sinusoidal stress), as well as the complex modulus $|E*|$ can be obtained by use of a ZNP automatic viscoelastometer over a wide temperature range. Hence, the modulus of energy stored is $E'=|E*|\cos\delta$, N/m^2; the modulus of dissipation is $E''=|E*|\sin\delta$, N/m^2; and the dissipation factor $\tan\delta = E''/E'$.

The experimental conditions were:

Size: length x width x height $= 2-5$ x $0.1-0.5$ x $0.01-0.2$ cm^3

Temperature increase: $2°C/min.$

Experimental temperature range: $-100°C - +160°C$

Experimental frequency: 3Hz.

2

Table 1.1 Composition of Samples (a).

样品(序号)(4) 含量(5) 组分(6)	NC	NG	安定剂(7)	助溶剂与工艺附加物(8)	Al	AP	HMX
1°	65.50	32.80	1.70				
	1	0.5	0.026				
2°	49.35	49.35	1.30				
	1	1	0.026				
3°	40.43	58.51	1.06				
	1	1.45	0.026				
4°	33.04	66.09	0.87				
	1	2	0.026				
5°	36.20	52.40	0.95	10.45			
	1	1.45	0.026	0.29			
6°	26.57	38.46	0.70	7.70	26.57		
	1	1.45	0.026	0.29	1		
7°	30.16	43.65	0.79	8.73		16.67	
	1	1.45	0.026	0.29		0.55	
8°	19.00	27.50	0.50	5.50	Al+AP+HMX = 47.5%		
	1	1.45	0.026	0.29			
9°	24.59	35.59	0.65	7.12	32.05		
	1	1.45	0.026	0.29	1.3		
10°	24.59	35.59	0.65	7.12		32.05	
	1	1.45	0.026	0.29		1.3	
11°	24.59	35.59	0.65	7.12			32.05
	1	1.45	0.026	0.29			: 3

(1) Size of particles used:

    Al   8.7 μm

    AP   86 μm

    HMX   92 μm

(2) The compositions in the table are defined as: weight % ratio of component content to NC content.

(3) The samples in the table were made by casting.

(4) Sample number

(5) Content

(6) Composition

(7) Stabilizer

(8) Solubilizing agent and specialized additive

3

Table 1.2 Compositions of samples (b).

含量/% 组分[3] 样品序号[1]	NC	NG	TA	DBP
12°	66.67		33.33	
13°	66.67			33.33
14°	66.67	33.33		

(1) Sample number

(2) Content (%)

(3) Composition

Note: The samples listed in the table were made by
pressurization.

Table 1.3 Composition of samples (c).

DB Propellant		PVC Propellant	
Composition	Content %	Composition	Content %
NC	55	PVC	12.5
NG	29.3	AP	70
Solubilizing Agent	10	Plasticizer	17.0
Stabilizer	3.0	Stabilizer	0.5
Trajectory Improver	0.9	Combustion Rate Adjustor	0.05 (added)
Specialized Additive	1.8		

(1) NC — Nitrocellulose

(2) PVC propellant made by casting

(3) DB propellant made by screw-squeezing

1.2.2 Impulse Method

The experimental instrument used was a pendulum impulser. The conditions were:

Potential energy of the pendulum: 10 kg-cm

Size (width) of the clamp mouth: 4.0 cm

Impulsive speed: 2.87 m/s

Sample size: 5.5 x 0.5 x0.5 cm^3 (there is no gap on the sample)

Experimental temperature range: -100°C - +30°C

Time the sample remains at constant temperature: 30 min.

The strength of the impulse, a, is calculated by:

$$a = \left(\frac{\text{work consumed by cutting the sample}}{\text{sample cross section}}\right)\left(\frac{kg\text{-}cm}{cm^2}\right)$$

2. Results

The experimental results are shown in Figures 3.1 - 3.12.
In Table 2.1, the glass-converting temperature T_g and β-converting temperature T_β, determined from the temperature corresponding to the maximum dissipation angle, are given.

Table 2.1 T_g and T_β of the different samples under 3Hz dynamic conditions.

1 样品序号	1°	2°	3°	4°	5°	6°	7°	8°
T_g/°C	84.2	52.4	34.0	25.6	31.1	32.4	31.0	31.2
T_β/°C	-29.5	33.7	-41.1	-46.5	36.0	-31.3	-36.8	-36.2
2 样品序号	9°	10°	11°	12°	13°	14°	DB	PVC
T_g/°C	31.8	33.7	32.3	39.8	53.1	110.2	65.1	-21.6
T_β/°C	-35.1	-34.4	-37.7	10.8°	-10.7	-16.3°	-9.7	—

(1) Sample number

(2) Sample number

*Obtained by drawing a tangent line

3. Discussion

Following the style of dynamic analyses, we use the tan δ - t figure to observe the internal dissipation, with the characteristic range of material visco-elastic behavior determined by the E' - t figure as follows:

3.1 Characteristic Dynamic Properties of CMDB Propellants

(1) Under the 3Hz dynamic conditions, it can be seen from Figure 3.1 and Table 2.1 that the glass-converting dissipation peaks of the three propellants are in different temperature ranges. The T_g (-21.6°C) of the PVC propellant is much lower than room temperature. Hence, at room temperature it will behave like rubber. The T_g (65.1°C) of the DB propellant is much higher than room temperature. Hence, it is a plastic material under normal (room) temperatures. The T_g of CMDB propellant is 31.2°C, close to room temperature. Therefore, it does not have a mechanical behavior typical of plastic or rubber, and in fact presents mainly a transition property.

(2) Also from Figure 3.1, both the DB and CMDB have a relatively strong secondary transition (β-transition or β-relaxation), but PVC does not behave in such a way. The main internal converting dissipation peak of CMDB reaches a maximum in the range from -50°C to +70°C, which is the normal temperature range for propellants' use. Also, CMDB has a relatively stronger β-relaxation for internal dissipation in the low temperature ranges. By viewing the entire temperature range of propellant usage, the internal dissipation of CMDB

6

propellant is relatively higher.

The authors of Ref. 3 concluded that CMDB propellant is suitable at the temperature and vibration conditions encountered over the ocean, and they applied it to the engine of the "sea javelin" missile. This showed that the great internal dissipation of the propellant was fully used.

(3) From Figure 3.2, E' of the CMDB propellant is obviously located between those of DB and PVC, over the temperature ranges from -100°C to +100°C. In the temperature
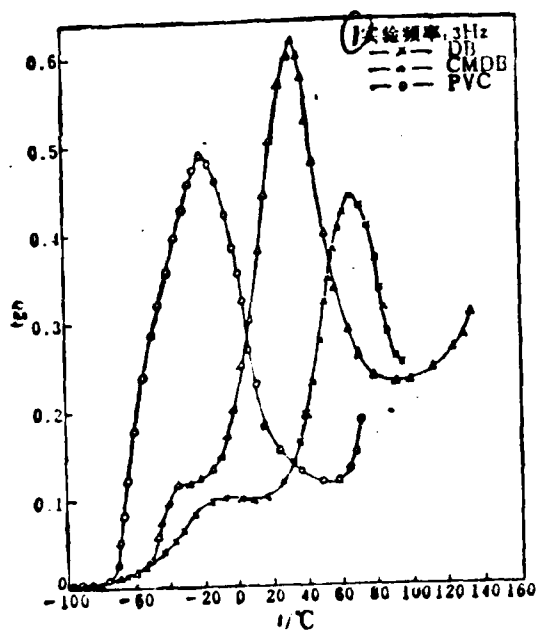

Figure 3.1 The tan δ - t curves for DB, CMDB and PVC propellants are shown. (1) Experimental frequency.
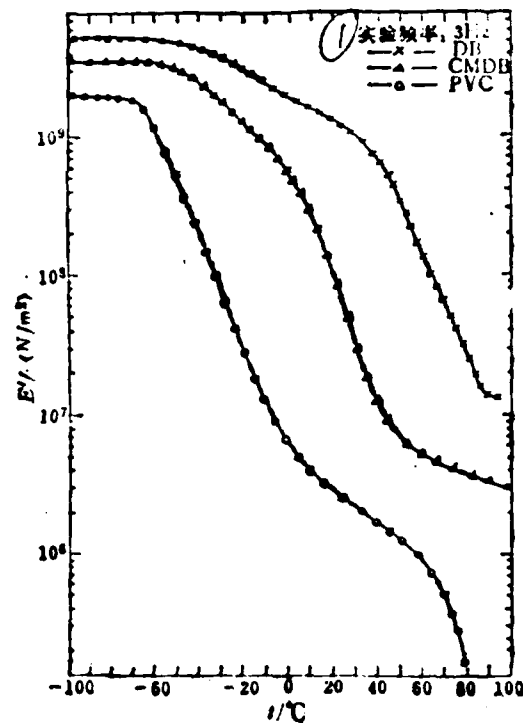
Figure 3.2 The E' - t curves of DB, CMDB and PVC propellant are shown. (1) Experimental frequency.

range of propellant use (-50°C to +70°C), CMDB propellant crosses the glass range (-50°C to +6°C), the glass conversion range (6°C to 50°C), and the highly elastic range (50°C to 70°C). Because of secondary transitions occurring above -60°C, relaxation occurs in the glass region and the value of E' continuously decreases. Therefore, with respect to the glass phase with constant modulus, it still behaves to some degree as a plastic in the low temperature range. Also, the transition region is very wide, with a decreasing modulus. The transition region occupies almost all of the usable temperature range (-50°C to +50°C) and this leads to a strong internal dissipation in the usable temperature range. The DB propellant crosses the glass phase region (-50°C to +40°C) and glass conversion region (40°C to 70°C) in its usable temperature range. Because of its high T_g, it is in the glass phase throughout the majority of its usable temperature range. Although β-relaxation occurs during its glass phase, distortions occur only with great difficulty because of a high, slowly decreasing value of E'. The PVC propellant is located basically in the glass-converting and the highly elastic regions where the temperature is between -50°C and +70°C. At the same time, because its Tg is low and its modulus decreases rapidly, it is a very good plastic propellant in its usable temperature range.

From the above analysis, the dynamic mechanical properties of the three propellants are seen to differ tremendously. This

is due mainly to their different basic structure (the CMDB and the DB propellants are NC, while the PVC propellant is polyvinyl chloride). For the same basic structure   the reasons for different properties would be the different forming method used (CMDB is made by casting and DB is made by screw-squeezing) and the different ratios of fiber to solution (DB: NC/solutions = 1.26, CMDB, NC/solution = 0.57). Lastly, there is a large amount of filler in CMDB.

3.2 The Relation Between Dynamic Mechanical Properties and the Anti-impulse Energy of CMDB

Recently, it has been proven by many experiments with [4-7] polymers that the impulsive strength below T_g will increase if the polymers have a strong ϱ-relaxation. From this experiment we know that the ϱ-relaxation of CMDB is relatively strong. Therefore, an impulse experiment was done to demonstrate the increase in impulsive strength in its glass phase.
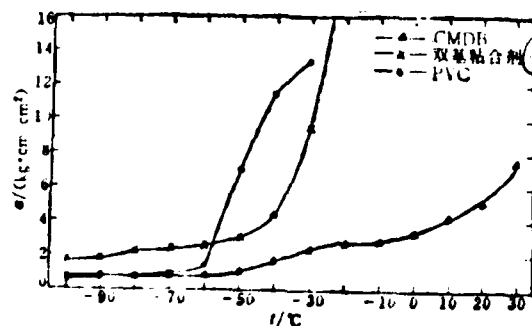

Figure 3.3   Curves showing a vs. t for the double-base adhesive and the CMDB and PVC propellants. (1) Double-base adhesive.

9

From Figure 3.3 it is seen that the impulsive strength of CMDB propellant increases in two stages as the temperature increases. Since its β-relaxation can yield great internal dissipation, much of the impulsive energy can be dissipated even under rapidly increasing temperatures. This temperature rise is caused by the great increase in the impulsive energy, which in turn is caused by the chain-motion. Hence, occurrence and development of cracks may be prevented or reduced and the resistance of CMDB to impulses will increase. From cross-sectional observations of the samples, the cross sections tended to be rougher and the brightness was reduced to zero when the temperature changed from -50^cC to -30^cC. It obviously forms the transitional characteristics from brittle cracks to tenacious cracks. Therefore, the cracks formed in CMDB propellant at temperatures above $-30°$C are tenacious.

Nielson [8] indicated that if E''/E' is lower than approximately 0.02, the tough polymers are usually brittle; i.e. the impulsive strength of the material is low. If E''/E' is greater than 0.1 the impulsive strength is usually high. From our experimental data in this paper, tan δ of CMDB propellants is higher than 0.02 at temperatures greater than or equal to $-52.6°$C. It is greater than 0.10 for temperatures greater than or equal to $-36.5°$C. Hence, CMDB propellants have a certain degree of tenacity with temperatures higher than $-52.6°$C, and subject to 3Hz dynamic conditions. It also has a relatively large impulsive strength at temperatures higher than $-36.5°$C.

From Figure 3.1 it can be seen that the above conclusions fall within its β-relaxation region. This temperature ($-36.5°C$) is consistent with its T_β ($-36.2°C$). The impulsive experiments have proven that β-relaxation is related to impulsive strength. Hence, it is possible to employ CMDB propellants between T_g and T_β.

A β-relaxation also exists in the double-base adhesive /54 (see Figure 3.4). Therefore, conclusions similar to those obtained for the CMDB propellant can be reached. However (Fig. 3.1), because the β-relaxation does not exist in PVC propellants, its impulsive strength will rapidly increase when the temperature increases to the major chain-motion condition ($-60°C$). Comparing this to CMDB, PVC can only be used at a temperature higher than its major chain-motion temperature T_g. Hence, it is inappropriate to consider the T_g of CMDB as the limit for its low temperature use. The influence of strong β-relaxation on the mechanical properties at low temperatures should be considered.

3.3 Influence of the Fillers to the Dynamic Mechanical Properties of the Double-base Adhesive

The influence of the fillers on the dynamic mechanical properties of the double-base adhesive is shown in Figures 3.4 - 3.6. It is seen from these figures that the value of tanδ corresponding to both the pure double-base adhesive sample (sample 5) and to the pure material with filler added (samples 6 - 11) increases at around $-60°C$ with a /55 strong β-relaxation. However, the two internal dissipation peaks of transition are not significantly shifted with the addition of the different fillers. Their transition

11

temperatures are very close to each other. The added fillers
significantly decrease the peak of β-internal dissipation.
The effects of the three fillers on the double-base adhesive
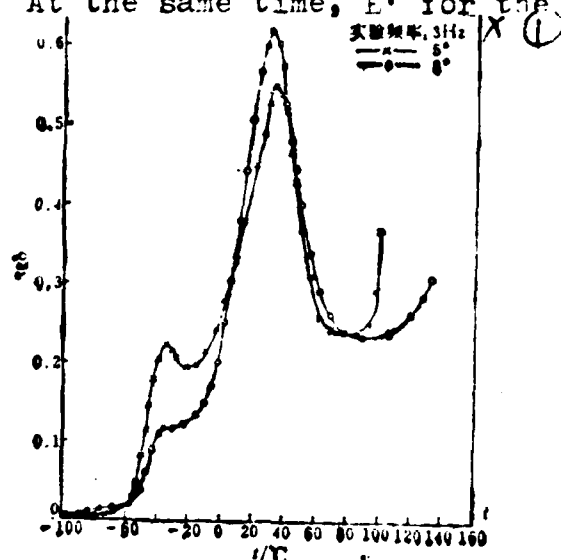are the same. At the same time, E' for the sample with the

Figure 3.4 The tan δ -t curves for
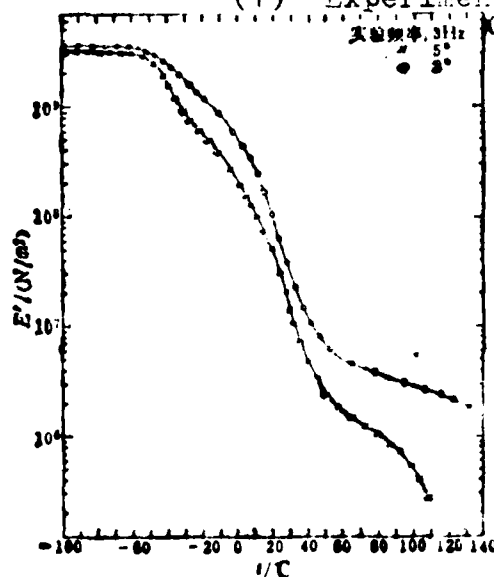sample numbers 5 and 8 are shown.
(1) Experimental frequency.

Figure 3.5 The E'-t curves for
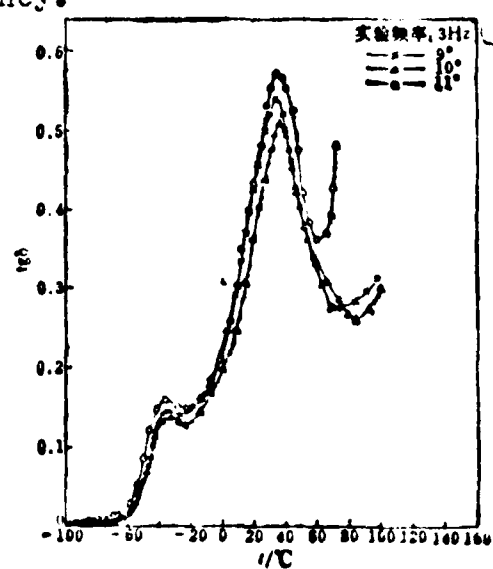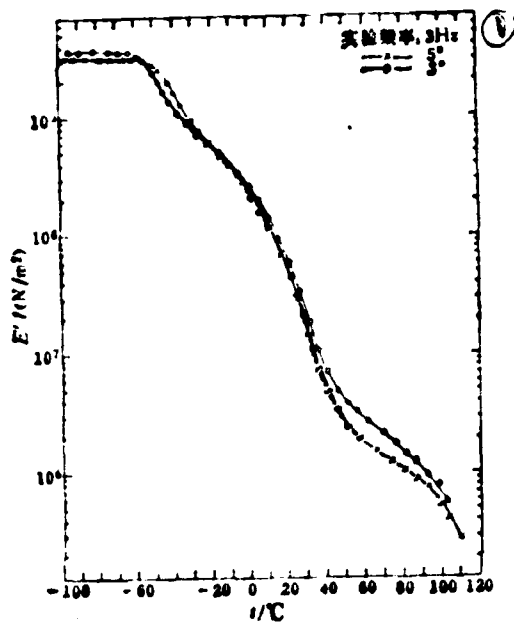sample numbers 5 and 8 are shown.
(1) Experimental frequency.

Figure 3.6 The tan δ -t curves
for sample numbers 9, 10 and 11
are shown. (1) Experimental
frequency.

12

added fillers is greater than that of the pure adhesive (with increasing temperature) after occurrence of β-relaxation (above -60 C). Also, E' is increased significantly in the highly elastic region. This statement is consistent with the dynamic mechanical properties of common polymers with added rigid fillers (Ref. 9), as well as the effects of the rigid fillers mentioned above on a complex and nitrified plasticsol (Refs. 10 and 11).

3.4 The Influence of Plasticizers to the Dynamic Mechanical Properties of the Double-base Adhesive

(1) The Influence of Solubilizing Agents and Specialized Additives

Sample number 3 is made of the double-base adhesive without solubilizing agents and other specialized additives. Comparing this to sample number 5 (Table 2.1, Figure 3.7), the effects of the small amount of solubilizing agent and the specialized additive on the dynamic mechanical properties and the two transition temperatures of the CMDB propellant is not significant.

3.7

The E'-t curves for
sample numbers 3 and 5
are shown. (1) Experi-
mental frequency.

3.8
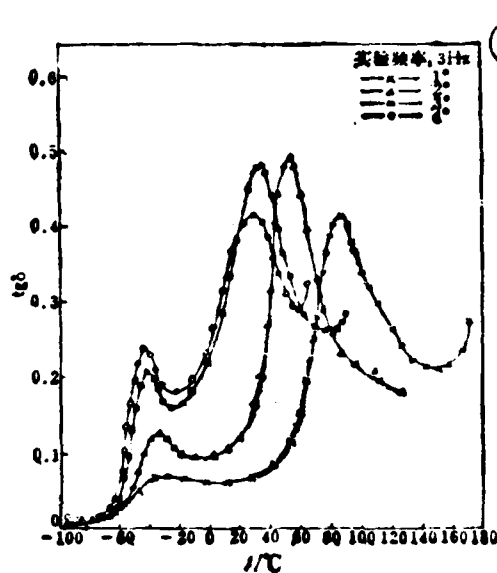
The tan δ-t curves for
sample numbers 1-4 are
shown. (1) Experimental
frequency.

(2) Influence of the Amount of NG (Figures
3.8 - 3.10)

The ratio of NG to NC varies from 0.5 to 2 for sample numbers 1 - 4. From figures 3.8 - 3.10, the decrease in T_f of an adhesive system caused by NG is not as great as the decrease in T_g (this is mainly due to the decrease in activity of NG molecules at low temperature). The major influence of NG on an adhesive system is the effect on the main transition, but the increase in plasticity is related to NG content. When the amount of NG reaches a certain level, 58.51% in the case of sample number 5, it reduces the T_g decrease in an adhesive system. This also narrows the highly elastic region and intensifies the decrease of frictional flow temperature T_t. This result is consistent with the rule [12] which generally describes the influence of adding plasticizers to rigid polymers. Hence, there exists an amount of plasticizer added to an adhesive system that results in an optimum plasticization. The highly elastic region is widest with this amount.

The optimum amount of NG can be determined by connecting NC. It has the ability to prevent the molecular chain from sliding. Hence, the amount of NG can be increased. It not only decreases the T_g but also widens the highly elastic region and solves the problem caused by unconnected NC. Also, NC can /56 increase the internal dissipation of the adhesive at low

14

temperatures. This helps to improve the impulsive resistance of CMDB propellants at low temperatures. Therefore, using preconnected NC to increase the plasticity, combined with adjusting the NG dosage, results in an effective way of improving the dynamic mechanical properties of CMDB propellants at low temperatures.
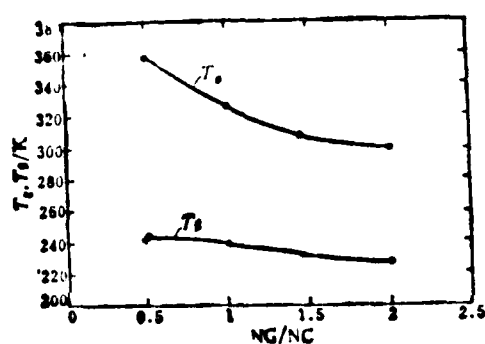

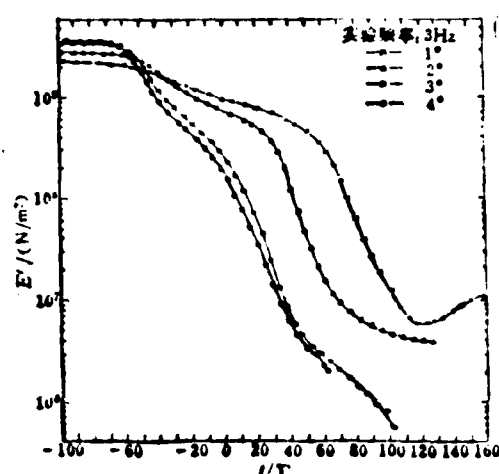Figure 3.9 The T_g (T_ϕ) — NG/NC curves of sample numbers 1 — 4 are shown.

Figure 3.10 The E'-t curves for sample numbers 1 — 4 are shown. (1) Experimental frequency.

(3) The Influence of Different Plasticizers

The experimental results from adhesive samples made of different plasticizers (TA, DBP and NG) and NC are shown in (12*,13*,14*) Table 2.1 and Figure 3.11. The results show that ρ-transition always appears, even for different kinds of plasticizers. (This indicates that ρ-transition is caused by motion of γ-relaxation unit of the same structure carrier as NC.) Also,

15

the decrease in T_g and E' of NC caused by NG is not as significant as those caused by TA and DBP for the same weight percentage. Therefore, the effectiveness of plasticization will be better if NG is combined with another plasticizer under conditions that do not influence the energy of CMDB propellants.
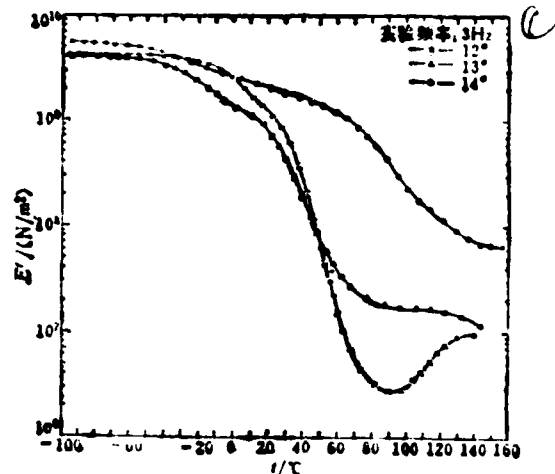

Figure 3.11   The E'-t curves for sample numbers 12 - 14 are shown.   (1)   Experimental frequency.

(4)   An Attempt at a Quantitative Description

From the equal viscosity theory, plasticizers and polymer systems can be treated as a dense solution of polymers. From Flory's formula for viscosity of a dense solution of macromolecules, a solution of the quantitative relation between the weight percentage W of a polymer and T_g of a dense solution, [13], is:

$$\sqrt{\overline{W}} = A' - \frac{E_v}{BRT_g}$$

where E_v is the viscous activation energy; T_g is the glassifying temperature; and A' and B are constants; assuming that E_v does

16

not vary with W. A double-base adhesive is a dense solution of NC. Therefore, the conditions described for the relation are satisfied. Under the constant viscous situation at T_g, E_V is very close to a constant. Hence, $(-E_V/BR)$ may be treated as a constant, equal to D. Therefore,

$$\sqrt{W'_{NC}} = A' + \frac{D}{T}$$

The values of $\sqrt{W_{NC}}$ and $1/T_g$ of sample numbers 1 - 4 are shown in Figure 3.12. Using linear regression, it is found that A' = 1.9625, D = -410.85, and the linear correlation coefficient is -0.99504. Therefore, the relation is very close to linear. When the weight percentage of NC is between 33.04 and 65.50% and the ratio stabilizer/NC = 0.0260, the emperical relation between $\sqrt{W_{NC}}$ and T_g for an adhesive system under $3H_z$ dynamic conditions is:

/57

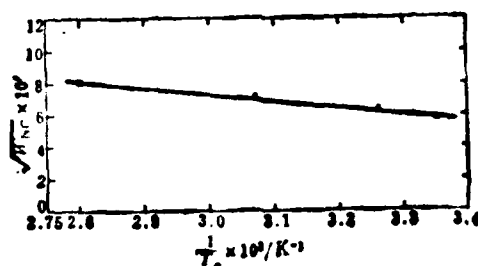$$\sqrt{W}_{NC} = 1.96 - 4.11 \times 10^2 \frac{1}{T_g}$$

Figure 3.12 The relation between $\sqrt{W_{NC}}$ and $1/T_g$ for sample numbers 1 - 4.

17

4. Conclusions

(1) The dynamic mechanical properties of CMDB propellants are between those of DB propellants and PVC complex propellants. In the usable temperature range, it crosses the glass-region (relaxation occurring), the glass conversion region and the highly elastic region. It has a very wide transition region. Therefore, its internal dissipation is relatively large over the entire usable temperature range. This aids the bearing of a great dynamic load during transportation, ignition, landing and flying.

(2) There is a strong β-relaxation for CMDB at temperatures below T_g. This improves the impulsive strength for temperatures between T_g and T_β and therefore improves the resistance to impulse of CMDB at low temperatures. This feature is very valuable in resisting the impulsive load caused by ignition.

(3) The dynamic mechanical properties of CMDB propellants mainly depend on its adhesive systems. The influence of solid fillers on the transition temperature (T_g, T_B) is not significant. They do increase the energy modulus E' (especially in the highly elastic region) and decrease the internal dissipation at low temperatures. Therefore, the deformability of CMDB will be reduced and the dynamic mechanical properties will be unfavorably affected.

(4) There exists an optimal amount for plasticization of the double-base adhesive. Below this value, the plasticization

18

effectiveness of NG increases significantly and at that value the highly elastic region is widest. For the same weight percentage, the decrease in T_g and E' of NC caused by NG is not as great as that caused by TA and DBP.

(5) The relation between $1/T_g$ and the square root of NC weight percentage, W_{NC}, of a double-base adhesive system is linear.

(6) Using a viscoelastometer to measure the dynamic mechanical properties of solid propellants over a wide temperature and frequency range, we have been able to observe the characteristic region of the visco-elastic behavior and have obtained the information on glass-conversion, secondary transition, internal mechanical dissipation and surface activation; these features are associated with molecular motion. This has been beneficial to research on the microscopic structures and the macroscopic behavior of propellants on the basis of molecular motion. At the same time, under the development and selection of the propellants for major strategic missiles, it is necessary to estimate the overall mechanical properties of solid propellants.

REFERENCES

1. Hufferd W.L. and Fitzgerald J.E., Development of a solid propellant viscoelastic dynamic model appendix a., N76-25433, (1976).

2. Kinloch A.J. and Gledhill R.A., Propellant failure: a fracture mechanic approach AIAA80-1180, (1980).

3. Gordon S. and Darwe H.M., Composite modified cast-double- base propellants technology and application 9th International Aeronautical Congress, 1969.

4. Kaufman H.S. 9ed), Introduction to polymer Science and technology, New York, Wiley-Interscience, 1977.

5. Nielsen L.E., Ding Jiading (translator). Mechanical Properties of Macromolecule and Complex Material, Light Industry Press, Beijing, p. 230, 1981.

6. Chengdu Institute of Science, Tianjing Institute of Light Industry and Beihing Institute of Chemical Engineering, The Chemistry and Physics of Macromolecules, Light Industry Press, Beijing, pp. 160-162, 1981.

7. Karger-Kocsis J. and Kuleznev V.N., _Polymer_ Vol. 23, No. 5, 699-705, (1982).

8. Nielsen L.E., Fang Zhiliu (translator), Mechanical Properties of Polymers, Shanghai Scientific and Technical Press, p. 198, 1965.

9. Nielsen L.E., _Appl. polymer Symposia_, No. 12, 249-265, (1969).

10. Cantey D.E., Solid propellant structural integrity investigations, dynamic response and failure mechanisms, AD-452689, (1965).

11. Cantey D.E., Solid propellant structural integrity investigations, dynamic response and failure mechanisms, AD-610615, (1965).

12. Rigong J., Lectures on the Basic Theory of Physics of Macromolecules, _Plastic_, _31_, 79-80, extra issue (1978).

13. Zongneng Q., _Chemistry Communica_, _257_, 1, (1985).

END

DTIC

7 — 86